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(54) **Synergistic biocidal composition.**

(57) A broad spectrum preservative composition which comprises (a) a formaldehyde donor and (b) a halopropynyl compound; formulations containing such compositions, particularly personal care and household products; and a method of inhibiting the growth of microorganisms which includes contacting said microorganisms with the preservative composition.

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SYNERGISTIC BIOCIDAL COMPOSITION

Background of the Invention

The need for effective and economical preservative compositions is well known. There are a wide variety of applications where inhibiting the growth of microorganisms is necessary, as for example personal care products such as shampoos, creams, lotions, cosmetics, soaps and household products such as laundry detergents, hard surface cleaners, and fabric softeners. The shelf life of these preparations depends on their resistance to microbial spoilage.

In addition, in many industrial applications, antimicrobial agents are useful in paint, wood, textiles, adhesives, sealants, leather, rope, paper pulp, plastics, fuel oil, and rubber and metal working fluids. The control of slime-producing bacteria and fungi in pulp and paper mills and cooling towers is a matter of substantial commercial importance.

Certain compounds have long been known to be useful as preservatives. For example, U.S. Patent 3,987,184 shows the use of 1,3-dimethylol-5,5-dimethylhydantoin (DMDMH) as a useful formaldehyde donor for the preservation of personal care products, cosmetics, and household and industrial products. While it is inexpensive and effective against a wide variety of bacteria, the rate of kill is slow in inhibiting fungi and yeasts.

On the other hand, compounds such as the halopropynyl carbamates are known for their fungicidal activity; however, they are extremely costly and, as a result, have only found applications in specialty areas where high costs can be justified.

Other commercially known preservatives include Quaternium-15 (Dowicil 200, a trademark of Dow Chemical Company). It has the disadvantage of being a solid product which must be solubilized in water before it can be used in the end product. In aqueous solution it exhibits pH drift and causes formulation problems, particularly with regard to viscosity and color.

Imidazolidinyl urea (Germall 115, a trademark of Sutton Laboratories) has virtually no fungicidal activity. The manufacturer of this product actually recommends that it be used with parabens to provide fungicidal action.

Formaldehyde in the free state, as in formalin, is effective only for short periods of time. In addition, it is inactivated by protein.

Admixtures of methylchloroisothiazolinone and methylisothiazolinone (Kathon CG, a trademark of Rohm & Haas) are unstable in the presence of organic sulfur compounds, ingredients commonly used in personal care products. They react also with peroxide impurities present in materials such as amine oxides.

2-Bromo-2-nitropropane-1,3-diol (Lexgard-Bronopol, a trademark of Inolex) has limited fungicidal activity and parabens are required to provide microbiological activity.

Alkyl parabens (e.g., methyl, ethyl and propyl) have limited bactericidal action. They are generally solubilized in oil since they are poorly soluble in water, leading to formulation difficulties for personal care and household products. They are often inactivated by commonly used material such as gelatin, methyl cellulose, and polyethylene glycol.

The development of an effective synergistic combination, inexpensive in price and having a broad spectrum activity, has long been sought. For example, in U.S. patent 4,454,146, a preservative composition having two components (the first being benzoic acid, formaldehyde or a mixture of isothiazolinone and a second component containing compounds with condensed aromatic rings) has been suggested for preservation applications. In addition, U.S. Patent 3,699,231 describes a synergistic mixture of sodium dimethyldithiocarbamate and formaldehyde for killing bacteria in drilling fluids; U.S. Patent 3,929,561 comprises mixtures of isothiazolinones and bis(trichloromethyl) sulfones for inhibiting the growth of slime for industrial purposes; and U.S. Patent 4,655,815 describes synergism between 2-bromo-2-bromomethylglutaronitril and a formaldehyde donor such as dimethyloldimethylhydantoin, hydroxyaminopropanol, hydroxyethylnitropropanediol, blends of hydroxymethyl azadioxabicyclooctane and hydroxymethylamino ethanol; chloroallyl triazoadamantine chloride, chloroallyl heximinium chloride and hexamethylene tetramine halo hydrocarbon quaternaries.

Unfortunately, the above compositions are not suitable for personal care and household products because of their unfavorable toxicity, particularly skin and eye irritation and/or incompatibility with commonly used ingredients.

Brief Description of the Invention

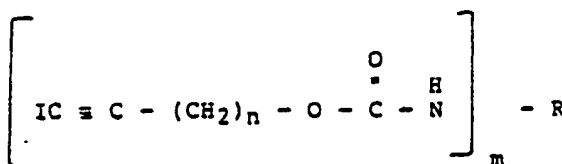
In accordance with the invention, it has now been discovered that a synergistic combination of a selected formaldehyde donor and an iodopropargyl compound gives both broad spectrum bactericidal and fungicidal activity suitable for use in personal care and household products. A particularly surprising aspect of the discovery is that an extremely small amount of the costly halopropynyl carbamate can be combined with the formaldehyde donor to give a composition that has particularly outstanding fungicidal activity. This activity could in no way be predicted based on the known biocidal effects of the components individually.

Relative proportions of the two components can vary widely and the optimum proportion would be affected by the various compounds selected as well as the desired application. It has been discovered that a total composition which contains as little as 1 part in 50 of the costly iodopropargyl compound will have a fungicidal activity exceeding that of an equal weight of the halopropynyl carbamate alone. This is particularly surprising since this enhancement is realized with formaldehyde donors which have essentially no fungicidal activity.

Detailed Description of the Invention

The first component of the synergistic composition of the invention may be selected from the known formaldehyde donors having chemical and physical characteristics compatible with use in personal care products. Such products must, of course, not be odiferous or an irritant or toxic when applied to the skin. Examples of such compounds include dimethyloldimethylhydantoin, N,N'-methylene bis [N'-{1-(hydroxymethyl)-2,5-dioxo-4-imidazolidinyl}urea] and N-(hydroxymethyl)-N-(1,3-dihydroxymethyl-2,5-dioxo-4-imidazolidinyl)-N'-(hydroxymethyl) urea; the cis isomer of 1-(3-chloroallyl)-3,5,7-triaza-1-azoniaadamantane chloride.

Examples of compounds which may be used as the second component of the invention are the fungicidally active iodopropargyl derivatives. These include compounds derived from propargyl or iodopropargyl alcohols such as the esters, ethers, acetals, carbamates and carbonates and the iodopropargyl derivatives of pyrimidines, triazolinones, tetrazoles, triazinones, sulfamides, benzothiazoles, ammonium salts, carboxamides, hydroxamates, and ureas. Preferred among these compounds is 3-iodo-2-propynyl-butyl carbamate, IPBC. This compound is included within the broadly useful class of compounds having the generic formula:



wherein R is selected from the group consisting of substituted and unsubstituted alkyl, aryl, and alkylaryl groups having from 1 to 20 carbon atoms, and m and n are independent integers from 1 to 3.

As noted above, the ratio of the two components varies depending on the application and the particular component selected. Broadly speaking, from 50:1 to 1:1 parts of the first to the second component may be used, preferably from 30:1 to 2:1, most preferably from 20:1 to 10:1, the parts being by weight.

The compositions of the invention have been found effective to inhibit the growth of bacteria, fungi and yeasts. Specifically, fungi and yeasts which may be inhibited include *Aspergillus niger*, *Candida albicans*, *Lentinus lepideus*, *Gloeophyllum trabeum*, *Corioulus versicolor*, *Trichoderma viride*, *Alternaria alternata*, *Penicillium decumbens*, *Botrytis cinerea*, *Colletotrichum coffeanum*, *Verticillium dahliae*, and *Trichophyton mentagrophytes*. Examples of the bacteria include *Salmonella choleraesuis*, *Serratia marcescens*, *Klebsiella pneumoniae*, *Enterobacter aerogenes*, *Aerobacter aerogenes*, *Bacillus subtilis*, *Proteus vulgaris*, *Streptococcus faecalis*, *Pseudomonas aeruginosa*, *Escherichia coli*, and *Staphylococcus aureus*.

The incorporation of the composition of the invention into personal care and household products is done in accordance with standard practices.

Typical personal care formulations, in addition to those described in the Examples, are set forth in the following tables:

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Personal Care Product		
Traditional All-Purpose Shampoo		
Ingredient	Percent (Wt)	Functionality
Sodium lauryl sulfate	35.00	Surfactant
Cocodiethanolamide	4.00	Viscosity builder
Sodium chloride	0.80	
Citric acid	0.17	
Preservative	q.s.	
Water, deionized	60.03	

The shampoo is prepared by dissolving the citric acid, sodium chloride, sodium lauryl sulfate and preservative in water and then adding the cocodiethanolamide, while stirring to insure homogeneity.

Personal Care Product		
Shampoo		
Ingredient	Percent (Wt)	Functionality
Sodium lauryl ether (2) sulfate	35.0	Surfactant
TEA lauryl sulfate	25.0	Surfactant
Cocodiethanolamide	3.0	Foam booster
Hydrolyzed animal protein	1.0	Conditioner
Preservative	q.s.	
Water, deionized	36.0	

To formulate this shampoo, all of the ingredients except the preservative are added to water and heated to 65° C. The preservative is added to achieve a clear solution while cooling to room temperature with stirring. If needed, the pH is adjusted to 7.0 with 50% citric acid and triethanolamine.

Personal Care Product		
Baby Shampoo		
Ingredient	Percent (Wt)	Functionality
Cocoamphocarboxyglycinate, sodium lauryl sulfate, and sodium laureth sulfate	20.0	Amphoteric surfactants and concentrates
Cocoamphocarboxyglycinate	10.0	Amphoteric surfactant
Sorbitan monolaurate mitigant (20) POE	5.0	Eye irritation
Polyethylene glycol 6000 distearate	1.3	Viscosity builder
Citric acid	0.3	
Preservative	q.s.	
Water, deionized	63.36	

In making this shampoo, the citric acid is dissolved in the water, the mixture heated and the remaining ingredients added in the order given. Polyethylene glycol 6000 distearate is dissolved at 75° C. The mixture is stirred while allowing it to cool to room temperature. The preservative is added at room temperature.

Personal Care Product		
Cationic Hair Conditioner		
Ingredient	Percent (Wt)	Functionality
Stearyldimethylbenzylammonium chloride	8.0	Conditioner
Hydrogenated starch hydrolysate	3.0	Humectant
Glyceryl monostearate, s.e.	1.0	Emulsifier, opacifier
POE-20 sorbitan tristearate	0.5	Emulsifier
Potassium chloride	0.4	
Preservative	q.s.	
Water, deionized	87.1	

In this formulation, half of the water is heated to 70 °C and glyceryl monostearate and POE-20 sorbitan tristearate are added with stirring. The quaternary salt, preheated to 70 °C, and the hydrogenated starch hydrolysate are added and stirring continued for 15-30 minutes. In a separate vessel, the potassium chloride is dissolved in the remainder of the water, heated to 65 °C and added to the rest of the batch. The emulsion is allowed to cool slowly to 40 °C with agitation.

Personal Care Product		
Conditioning Hair Mousse		
Ingredient	Percent (Wt)	Functionality
Acetamide MEA	5.0	Lubricant
Stearalkonium chloride	4.5	Conditioner
Sodium lauryl sulfate	3.5	Emulsifier
Hydrogenated starch Hydrolysate	5.0	Humectant
Polyquaternium-11	4.0	Holding power
Polyquaternium-10	0.7	Holding power
Lauryl alcohol (23) ethoxylate	0.5	Solubilizer
Preservative	q.s.	
Water, deionized	76.5	

The Polyquaternium-10 is dispersed in water with mild agitation and heated to 70 °C. The stearylalkonium chloride, sodium lauryl sulfate, hydrogenated starch hydrolysate, Polyquaternium-11 and the ethoxylated lauryl alcohol are added one at a time and mixed well after addition. The blend is cooled with mild agitation and the preservative added.

Personal Care Product		
Water Repellent Sunscreen		
Ingredient	Percent (Wt)	Functionality
Phase A		
Myristyl propionate	2.0	Emollient
Silicone fluid	10.0	Repellent
Octyl dimethyl p-aminobenzoic acid	5.0	Sunscreen
Glyceryl stearate	1.5	Emulsifier, opacifier
Stearic acid, triple pressed	3.5	Emulsifier for soap
Mink oil	5.0	Skin conditioner
Phase B		
Hydrogenated starch hydrolysate	5.0	Humectant
Triethanolamine	1.0	Emulsifier for soap
Preservative	q.s.	
Water, deionized	66.7	

The ingredients for Phases A and B, without the preservative, are mixed in separate vessels. The phases are melted at 75 °C, and mixed by adding Phase B slowly to Phase A with stirring. The mixture is cooled to room temperature while the stirring is continued. The preservative is added during the cooling cycle.

The following are examples of household products:

Household Product		
Light Duty Liquid Detergent		
Ingredient	Percent (Wt)	Functionality
Sodium lauryl ether sulfate (60%)	14.50	Surfactant
Sodium linear alkyl sulfonate (60%)	28.50	Surfactant
Cocodiethanolamide	4.50	Viscosity builder
Citric acid (50%)	0.15	
Preservative	q.s.	
Water, deionized	52.35	

The ingredients are combined with water in the order listed and stirred after the addition of each until a clear solution is formed.

Household Product		
Fine Fabric Detergent		
Ingredient	Percent (Wt)	Functionality
Myristamine oxide	5.00	Foam booster
Cocodiethanolamide	2.00	Viscosity foam booster
Sodium linear alkylate sulfonate, 60%	15.00	Surfactant
Sodium alpha olefin sulfonate, 40%	25.00	Surfactant
Citric acid, anhydrous	0.25	
Preservative	q.s.	
Water	52.75	

The citric acid is dissolved in the water and, with agitation, the remaining ingredients added in the order

listed until the product is homogeneous.

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Household Product		
Fabric Softener		
Ingredient	Percent (Wt)	Functionality
Ditallowdiamido methosulfate or	4.0	Softener Emulsifier and opacifier
Ditallowdimethyl ammonium chloride	4.0	
PEG stearate 400	1.5	
Preservative	q.s.	
Water	96.0	

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The quaternary salts, the preservative and the water are mixed until homogeneous.

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Household Product		
Solid Gel Room Deodorizer		
Ingredient	Percent (Wt)	Functionality
Tragacanth gum or Locust bean gum	15.0	Thickener
Preservative	q.s.	
Water	85.0	

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To prepare this product, the preservative is added to the water and then the thickener gradually added while stirring on low speed using an Oster blender. The speed is increased to high until the material takes on the appearance of petroleum jelly. It is transferred to a suitable container by first heating to 55 °C.

The synergistic composition is blended with a personal care or household products as exemplified above. Generally the total preservative present will be from 0.01 to 1.0% by weight, most preferably from 0.01 to 0.4%.

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In formulating the composition, naturally, the amount of the synergistic combination must be sufficient to be effective against the microorganisms which must be inhibited. Such minimum inhibitory concentrations can be readily determined by simple laboratory experimentation using standardized testing techniques.

In order to more fully illustrate the invention, attention is directed to the following example:

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Example

To demonstrate the microbiological effects produced by the synergistic composition, a cream and a lotion formulation were prepared. The dimethyloldimethylhydantoin (DMDMH) and 3-iodo-2-propynylbutyl carbamate (IPBC) were added at various use levels and microbiological challenge tests were conducted.

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The cream had the following composition:

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Ingredient	Percent by Weight
PEG-20 Glyceryl stearate	4.0
Glyceryl monostearate	6.0
Cetearyl alcohol (TA 16185)	1.5
Myristyl propionate	8.0
Glycerine, 99%	5.0
Water, deionized	75.5

To prepare the cream, the oil phase was first solubilized at 60-65 °C. The water phase (glycerine and water) was heated to the same temperature and added to the oil phase with mixing. The temperature was maintained at 48-52 °C. and the preservative system was added. The product was cooled with stirring to room temperature.

The lotion had the following composition:

Ingredient	Percent (W)	Functionality
Phase A		
Stearic acid USP/NF	3.0	Emulsifier
Myristyl propionate	2.0	Emollient
Glyceryl monostearate	1.5	Emulsifier
Cetyl alcohol	1.0	Secondary emulsifier
Ethoxylated (5) lanolin alcohols	0.5	Emollient
Ethoxylated (25) lanolin alcohols	0.3	Emulsifier
Phase B		
Hydrogenated starch hydrolysate	5.0	Humectant
Triethanolamine (99%)	0.4	Emulsifier
Preservative	q.s.	
Water, deionized	85.3	
Phase C		
Hydrolyzed animal protein	1.0	Moisturizer

To prepare the lotion (known as a TEA stearate lotion), Phase A and Phase B were heated separately to 65 °C. Phase C was then added to Phase A with mixing and the mixture added to Phase B at 60 °C. The preservative was added at this latter temperature. If necessary, the pH of the mixture is adjusted to 7.0 with 50% acetic acid and the lotion cooled to room temperature with stirring to complete the formulation.

Microbiological challenge tests were carried out by first inoculating forty gram aliquots of the formulation containing various amounts of preservative with *Candida albicans* (ATCC No. 10231) and *Aspergillus niger* (ATCC No. 16404) at concentrations of approximately 5×10^6 organisms per gram of formulation. The temperature of the samples was kept at 48-52 °C where sample viscosity was sufficiently low to insure homogeneous distribution of organisms after inoculation. Samples were incubated at 18-22 °C for a total of 7 days. A one ml. aliquot was taken from each sample on 0, 1, 2, 3 and 7 days, and diluted stepwise down to a 10^6 reduction in concentration. Each diluted sample was plated out in mycophil agar medium and incubated for three to seven days at 20-25 °C. After incubation, readings of the number of colonies per milliliter (cfu/ml) were made from the 0 to 7 day samples. The data are presented in Tables 1 to 3.

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Table 1

Synergistic Effects of DMDMH and IPBC
Candida Albicans in GMS Cream

	<u>System No.</u>	<u>DMDMH %</u>	<u>IPBC %</u>	<u>Total Wt., %</u>	<u>Ratio DMDMH/IPBC</u>	<u>Counts 3 Days CFU</u>
10	30	0.00	0.00	0.00		2,000,000
	26	0.22	0.00	0.22		600,000
	5	0.00	0.0244	0.0244		900
15	1	0.22	0.0244	0.2444	9.02	< 10
	26	0.22	0.00	0.22		600,000
	10	0.00	0.0122	0.0122		20,000
	6	0.22	0.0122	0.2322	18.03	< 10
20	26	0.22	0.00	0.22		600,000
	15	0.00	0.0061	0.0061		500,000
	11	0.22	0.0061	0.2261	36.06	200
	26	0.22	0.00	0.22		600,000
25	20	0.00	0.0030	0.0030		700,000
	16	0.22	0.0030	0.2230	73.33	2,000
	27	0.165	0.00	0.165		2,000,000
	5	0.00	0.0244	0.0244		900
	2	0.165	0.0244	0.1894	6.76	< 10
30	27	0.165	0.00	0.165		2,000,000
	10	0.00	0.0122	0.0122		20,000
	7	0.165	0.0122	0.1772	13.52	< 10
	27	0.165	0.00	0.165		2,000,000
35	15	0.00	0.0061	0.0061		500,000
	12	0.165	0.0061	0.1671	27.05	20
	28	0.11	0.00	0.11		900,000
	5	0.00	0.0244	0.0244		900
	3	0.11	0.0244	0.1344	4.51	< 10
40	28	0.11	0.00	0.11		900,000
	10	0.00	0.0122	0.0122		20,000
	8	0.11	0.0122	0.1222	9.02	< 10
	28	0.11	0.00	0.11		900,000
45	15	0.00	0.0061	0.0061		500,000
	13	0.11	0.0061	0.1161	18.03	1,100
	28	0.11	0.00	0.11		900,000
	20	0.00	0.0030	0.0030		700,000
	18	0.11	0.0030	0.1130	36.66	8,000
50	29	0.055	0.00	0.055		4,000,000
	5	0.00	0.0244	0.0244		900
	4	0.055	0.0244	0.0794	2.25	< 10

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Table 1 (Cont.)

System No.	DMDMH %	IPBC %	Total Wt., %	Ratio DMDMH/IPBC	Counts 3 Days CFU
29	0.055	0.00	0.055		4,000,000
10	0.00	0.0122	0.0122		20,000
9	0.055	0.0122	0.0672	4.51	< 10
29	0.055	0.00	0.055		4,000,000
15	0.00	0.0061	0.0061		500,000
14	0.055	0.0061	0.0611	9.02	200

Table 2

Synergistic Effects of DMDMH and IPBC Candida Albicans in TEA Stearate Lotion					
System No.	DMDMH %	IPBC %	Total Wt., %	Ratio DMDMH/IPBC	Counts 3 Days CFU
7	0.00	0.0000	0.000		7,000,000
8	0.22	0.0000	0.2200		2,000
11	0.00	0.0122	0.0122		20,000
1	0.22	0.0122	0.2322	18.03	<10
8	0.22	0.0000	0.2200		2,000
12	0.00	0.0061	0.0061		40,000
2	0.22	0.0061	0.2261	36.06	<10
9	0.165	0.0000	0.165		4,000,000
11	0.00	0.0122	0.0122		20,000
3	0.165	0.0122	0.1772	13.52	<10
9	0.165	0.0000	0.165		4,000,000
12	0.00	0.0061	0.0061		40,000
4	0.165	0.0061	0.1711	27.05	<10
10	0.11	0.0000	0.11		7,000,000
11	0.00	0.0122	0.0122		20,000
5	0.11	0.0122	0.1222	9.02	<10
10	0.11	0.0000	0.11		7,000,000
12	0.00	0.0061	0.0061		40,000
6	0.11	0.0061	0.1161	18.03	<10

Table 3

Synergistic Effects of DMDMH and IPBC Aspergillus Niger in GMS Cream					
System No.	DMDMH %	IPBC %	Total Wt., %	Ratio DMDMH/IPBC	Counts 1 Day CFU
30	0.00	0.00	0.00	4.51	200,000
28	0.11	0.00	0.11		30,000
5	0.00	0.0244	0.0244		3,000,000
3	0.11	0.0244	0.1344		<10
28	0.11	0.00	0.11	9.02	30,000
10	0.00	0.0122	0.0122		700,000
8	0.11	0.0122	0.1222		<10

It will be noted from the above tables that the synergistic combination of the invention is considerably better than either of the components with regard to the microorganisms tested.

Claims

1. A preservative composition which comprises an admixture of (a) a nontoxic, nonodiferous formaldehyde donor and (b) a halopropynyl compound.

2. The composition of claim 1 wherein the admixture contains dimethyloldimethylhydantoin and 3-iodo-2-propynylbutyl carbamate.

3. The composition of claim 1 wherein component (a) is imidazolidinyl urea, imidazolidinyl urea II or Quaternium 15.

4. The composition of claim 1 wherein component (b) is 3-iodo-2-propynylbutyl carbamate.

5. The composition of claim 1 wherein the weight ratio of component (a) to (b) is from 50:1 to 1:1.

6. The composition of claim 1 wherein the weight ratio of component (a) to (b) is from 20:1 to 10:1.

7. A personal care composition which comprises a surface active agent containing an effective amount of the composition of claim 1.

8. The personal care composition of claim 7 wherein the composition is a skin cream, a lotion, a shampoo, or a soap.

9. A household product composition which comprises a surface active agent containing an effective amount of the composition of claim 1.

10. The household product composition of claim 9 wherein the composition is a detergent, a hard surface cleaner, a fabric softener, or a room deodorizer.

11. A method of inhibiting the growth of microorganisms which comprises contacting said organisms with the composition of claim 1.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 89 30 0468

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
D,A	US-A-3 987 184 (D.H. FOELSCH) * Whole document *	1-11	A 01 N 47/36 A 01 N 47/28
A	EP-A-0 194 466 (GIULINI CHEMIE) * Claims *	1-11	A 01 N 47/12 A 61 K 7/48 A 61 K 7/06
A	WO-A-8 402 058 (SUTTON LABS.) * Whole document *	1-11	C 11 D 3/48 // (A 01 N 47/36 A 01 N 47:12)
A	CHEMICAL PATENTS INDEX, BASIC ABSTRACTS JOURNAL, section C, AGDOC, week 8625, 13th August 1986, no. 86-158774/25, Derwent Publications Ltd, London, GB; & JP-A-86 091 109 (SANYO MOKUZAI) -----	1-11	(A 01 N 47/28 A 01 N 47:12) (A 01 N 47/12 A 01 N 43:90 A 01 N 43:50)
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			A 01 N A 01 K C 11 D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 12-05-1989	Examiner FLETCHER A.S.
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- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
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- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☒ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
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